

Glass Science and Technology 3

Properties and Applications of Glass

HAROLD RAWSON

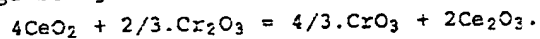
*Department of Ceramics, Glasses and Polymers,
University of Sheffield, England*



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When dealing with redox pairs which lie closer together, the Ellingham diagram is of little value for predicting what will happen when they are brought together in a glass. Thus the diagram predicts that CeO_2 will oxidize Cr_2O_3 to CrO_3 , the free energy change being -10 K Cal for the reaction



However, although the equilibrium is to the right in a sodium aluminoborate glass it is to the left in a soda-lime-silica glass.

To be able to understand the interaction of redox pairs in glasses of various compositions, one needs information about the free energy changes that occur when the oxides are dissolved in the glass in question. Expressed in another way, one needs to know the activities of each ion. Douglas (1974) has discussed some of the available experimental results in terms of the probable changes of chemical potential which occur when oxides are dissolved in glass and he develops a modified Ellingham diagram which gives a convenient pictorial representation of the changes that occur and of the changes in the equilibria to be expected as the glass is cooled. These considerations are of considerable interest and may be correct, but much more experimental work is clearly needed before a completely satisfactory account can be given of the behaviour of transition metal ions in glass.

D. The Absorptivity of Oxide Glasses in the Ultra-Violet

The absorption of ultra-violet radiation by oxide glasses has been referred to in the previous chapter during the discussion of the dispersion properties.

As one moves into the UV from the visible, the absorption coefficient of oxide glasses begins to rise rapidly and most of these materials are effectively opaque at wavelengths shorter than 200 nm in thicknesses of a millimetre or so. The rapid rise of absorption coefficient is referred to as the "UV cut off" and many studies have been made of the effect of composition on the wavelength at which it occurs. The results of work of this kind are, of course, valuable in the development of UV transmitting glasses for such applications as bactericidal lamps. The interpretation of the results is complicated by the fact

that the increase in absorption in the UV is determined partly by the major components of the glass composition and partly by impurities, in particular the oxides of iron, chromium and titanium which may be present at levels of only a few parts per million. The ions Fe^{3+} , Cr^{3+} and Ti^{3+} absorb very strongly in the ultra-violet. Thus the molar absorptivity of Fe^{3+} in a silicate glass is approximately $3,000 \text{ l mole}^{-1} \text{ cm}^{-1}$ and is centred at about 210 nm. This is about one hundred times greater than the absorptivities characteristic of the electron transitions referred to in the previous section. The electron transitions responsible for these strong absorptions are called charge transfer transitions because they are believed to involve excitations in which an electron leaves an orbital mainly located on one ion, e.g. an Fe^{3+} ion to occupy an orbital mainly located on a nearby ion, e.g. one of the nearest-neighbour oxygen ions (or vice versa).

Since, as we have seen, a change in glass composition affects redox equilibria such as $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{Cr}^{3+}/\text{Cr}^{6+}$, it is difficult to decide whether a shift in the UV cut off is associated with electron transitions in the ions which form the major part of the glass structure or is merely due to changes in the valence state of impurity ions. Only relatively recently has work been done on glasses made from sufficiently pure raw materials to be reasonably certain that composition effects on the UV cut off can be attributed to transitions involving the major constituents of the glass (Sigel, 1973). As stated in the previous chapter, the main effect of increasing the alkali content of a silicate or borate glass is to move the UV cut off to longer wavelengths. It appears to be generally accepted that the first strong absorption encountered on moving to shorter wavelengths in the UV involves the excitation of an electron from valence levels on oxide ions to higher levels localized on the same ions. Also, for non-bridging oxygens the excitation energy is less than for bridging oxygens; consequently the absorption occurs at a longer wavelength.

Since it is clearly impossible to study the UV-absorption spectra directly because of the high absorptivity of oxide glasses in this region (10^4 - 10^6 cm^{-1}), indirect methods must be used. A certain amount of information is available on the var-

ation of the reflectivity of oxide glasses with wavelength in the UV. From the results of experiments of this kind it is possible to calculate the variation of absorptivity with wavelength. For oxide glasses, the wavelengths of the absorption maxima are fairly close to the wavelengths of the reflectivity maxima. Figure 118 shows the results of Philipp (1966) for

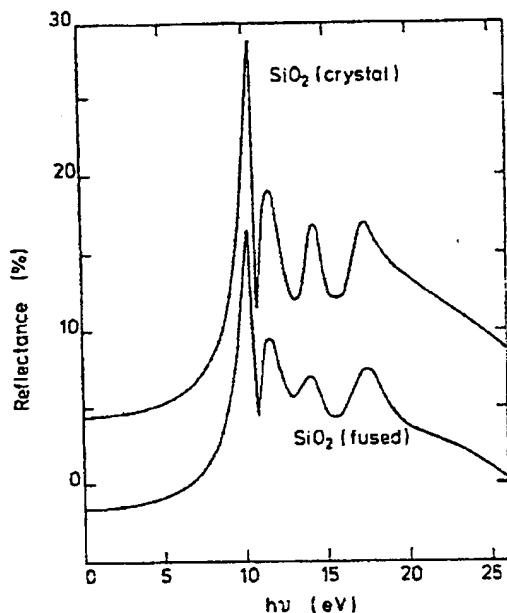


Fig. 118. Reflection spectra of crystalline and vitreous silica.

α -quartz and vitreous silica. Note that the reflection maxima occur at practically the same energy values (or wavelengths) for both materials. The absorption maxima occur at wavelengths (calculated from these results) of 10.2, 11.7, 14.3 and 17.2 eV. The wavelength corresponding to the lowest energy peak is 121.5 nm. This is a wavelength significantly less than that of the UV cut off for high purity vitreous silica which is about 160 nm. Sigel (1973) has measured the reflection spectra of various two- and three-component alkali silicate glasses and has observed additional maxima at 8.5 eV (146 nm) and 9.3 eV (133 nm). The position of these maxima is practically independent of the nature of the alkali.